

**Proposals for a globally harmonized system of classification  
of chemicals presenting physical hazards**

**NOTE 1:** This annex has been prepared by the secretariat on the basis of the results obtained by the Working Group by consensus in 1995, 1996 and 1997 (ST/SG/AC.10/23/Add.4, ST/SG/AC.10/C.3/26/Add.3 and ST/SG/AC.10/C.3/28/Add.2, annex 1).

**NOTE 2:** The term "Manual of Tests and Criteria", wherever it is used in this Annex, means the second revised edition of the United Nations Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria (ST/SG/AC.10/11/Rev.2).

**1. Proposal for definitions of gases, liquids and solids**

Definitions	
Definition of gases and gas mixtures (substances, mixtures and solutions with a lower vapour pressure are regarded as liquids)	Vapour pressure at 50 EC > 300 kPa or completely gaseous at 20 EC (at standard pressure of 101.3 kPa)
Definition of liquids (substances not falling under this definition are regarded as solids)	Melting point # 20 °C at 101.3 kPa or for viscous substances without a defined melting point, test according to ASTM D 4359-90 or penetrometer test as prescribed in Annex A.3 of the ADR 1/ with penetrometer according to ISO 2137:1985

1/ European Agreement concerning the International Carriage of Dangerous Goods by Road (ECE/TRANS/115, United Nations publication Sales No. E.96-VIII-2).

**2. Proposal concerning test conditions**

- 2.1 Screening procedures may be used to determine if full scale testing to assess physical hazard of a substance is necessary

**NOTE:** Screening procedures<sup>1/</sup> have been developed by the UN Committee of Experts on the Transport of Dangerous Goods as voluntary guidance to minimize the cost of testing products.

- 2.2 For classification tests on solid substances, the tests should be performed on the substance as presented. If for example, for the purposes of supply or transport, the same chemical is to be presented in a different physical form which is considered likely to materially alter its performance in a classification test, the substance must be tested also in the new form.

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<sup>1/</sup> ST/SG/AC.10/C.3/28, annex 2 (subject to endorsement by the Committee at its twentieth session (7-16 December 1998)). After endorsement by the Committee, the screening procedures should be published by the United Nations either as an addendum to the Manual of Tests or Criteria or by incorporation in the third revised edition of the Manual.

### 3. Proposals concerning flammability

#### 3.1 Proposal for hazard levels for the classification of flammable liquids

Hazard level	Criteria	Test methods
Very high danger	Initial boiling point # 35 EC and flash point < 23 EC	Closed cup methods to be used, open cup methods only acceptable in special cases
High danger	Flash point < 23 EC and initial boiling point > 35 EC	
Medium danger	Flash point \$ 23 EC and # 60 EC	
Low danger	Flash point > 60 °C and # 93 EC	

**NOTE 1:** Gas oils, diesel and light heating oils in the flash point range of 55 °C to 75 °C may be regarded as a special group for some regulatory purposes.

**NOTE 2:** Liquids with a flash point of more than 35 °C may be regarded as non-flammable liquids for some regulatory purposes (e.g. transport) if negative results have been obtained in the combustibility test L.2 of the Manual of Tests and Criteria.

### 3.2 Proposal for hazard levels for the classification of flammable solids

Hazard level	Criteria	Test methods
High danger	-	-
Medium danger	<p>Screening test: testing time 2 min (20 min for metal powders)</p> <p>Burning rate test:</p> <p>Substances other than metal powders: wetted zone does not stop fire and burning time &lt; 45 s or burning rate &gt; 2.2 mm/s</p> <p>Metal powders: burning time <math>\neq</math> 5 min</p>	Method as described in section 33.2.1 of the Manual of Tests and Criteria
Low danger	<p>Method and test as described above</p> <p>Burning rate test</p> <p>Substances other than metal powders: wetted zone stops the fire for at least 4 min and burning rate &lt; 45 s</p> <p>Metal powders : burning time &gt; 5 min and <math>\neq</math> 10 min</p>	

### 3.3 Proposal for hazard levels for the classification of flammable gases

Hazard level	Criteria and test methods
High danger	<p>Gases and gas mixtures, which at 20 EC and a standard pressure of 101.3 kPa,</p> <p>(a) are ignitable when in a mixture of 13 % or less by volume in air; or</p> <p>(b) have a flammable range with air of at least 12 percentage points regardless of the lower flammable limit. Flammability should be determined by tests or by calculation in accordance with methods adopted by ISO (see ISO 10156:1996). Where insufficient data are available to use these methods, tests by a comparable method recognized by the competent authority may be used.</p>
Medium danger	Gases or gas mixtures, other than those of high danger, which, at 20 EC and a standard pressure of 101.3 kPa, have a flammable range in mixture in air.
Low danger	Not applicable

*NOTE: Ammonia and methyl bromide may be regarded as special cases for some regulatory purposes.*

### 3.4 Proposal for the definition of aerosols and criteria for their classification

"Aerosols, this means aerosol dispensers, are any non-refillable receptacles made of metal, glass or plastics and containing a gas compressed, liquefied or dissolved under pressure, with or without a liquid, paste or powder, and fitted with a release device allowing the contents to be ejected as solid or liquid particles in suspension in a gas, as a foam, paste or powder or in a liquid state or in a gaseous state."

Criteria for flammability remain to be developed.
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## 4. Proposals concerning reactivity

### 4.1 Proposal for the definition of pyrophoric substances and criteria for hazard levels for their classification

#### 4.1.1 Definition

Pyrophoric substances are solid or liquid substances which, even in small quantities, are liable to ignite within a short period of time after coming into contact with air.

**4.1.2 Criteria for hazard levels**

<b>Pyrophoric substances (liquids)</b>		
<b>Hazard level</b>	<b>Criteria</b>	<b>Test methods</b>
High danger	The liquid ignites in the first part of the test, or if it ignites or chars the filter paper.	UN Test N.3 Manual of Tests and Criteria (para. 33.3.1.5.4)
Medium danger	Not applicable	Not applicable
Low danger	Not applicable	Not applicable

<b>Pyrophoric substances (solids)</b>		
<b>Hazard level</b>	<b>Criteria</b>	<b>Test methods</b>
High danger	The sample ignites in one of the tests.	UN Test N.2 Manual of Tests and Criteria (para. 33.3.1.4.4)
Medium danger	Not applicable	Not applicable
Low danger	Not applicable	Not applicable

**4.2 Proposal for the definition of self-heating substances and criteria for hazard levels for their classification****4.2.1 Definition**

Self-heating substances are solid or liquid substances other than pyrophoric substances which, in contact with air and without energy supply, are liable to self-heating; these substances will ignite only when in large amounts and after long periods of time.

**4.2.2 Criteria for hazard levels**

<b>Self-heating substances</b>		
<b>Hazard level</b>	<b>Criteria</b>	<b>Test methods</b>
High danger	Not applicable	Not applicable
Medium danger	Positive result in a test using a 25 mm sample cube at 140 °C	UN Test N. 4 Manual of Tests and Criteria (para. 33.3.1.6.4.3)
Low danger	<p>(a) A positive result is obtained in a test using a 100 mm sample cube at 140 °C and a negative result is obtained in a test using a 25 mm cube sample at 140 °C <u>and</u> the substance is to be packed in packages with a volume of more than 3 m<sup>3</sup>;</p> <p>(b) A positive result is obtained in a test using a 100 mm sample cube at 140 °C and a negative result is obtained in a test using a 25 mm cube sample at 140 °C, a positive result is obtained in a test using a 100 mm cube sample at 120 °C <u>and</u> the substance is to be packed in packages with a volume of more than 450 litres;</p> <p>(c) A positive result is obtained in a test using a 100 mm sample cube at 140 °C and a negative result is obtained in a test using a 25 mm cube sample at 140 °C <u>and</u> a positive result is obtained in a test using a 100 mm cube sample at 100 °C</p>	UN Test N. 4 Manual of Tests and Criteria (para. 33.3.1.6.4.4)

**4.3 Proposal for the definition of substances which, in contact with water, emit flammable gases, and criteria for hazard levels for their classification****4.3.1 Definition**

Substances, which in contact with water, emit flammable gases are solid or liquid substances which, by interaction with water, are liable to become spontaneously flammable or to give off flammable gases in dangerous quantities.

### 4.3.2 *Criteria for hazard levels*

<b>Substances which, in contact with water, emit flammable gases</b>		
<b>Hazard level</b>	<b>Criteria</b>	<b>Test methods</b>
High danger	Any substance which reacts vigorously with water at ambient temperatures and demonstrates generally a tendency for the gas produced to ignite spontaneously, or which reacts readily with water at ambient temperatures such that the rate of evolution of flammable gas is equal to or greater than 10 litres per kilogram of substance over any one minute	UN Test N.5 Manual of Tests and Criteria (para. 33.4.1.4.4.2)
Medium danger	Any substance which reacts readily with water at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 20 litres per kilogram of substance per hour, and which does not meet the criteria for high danger	UN Test N.5 Manual of Tests and Criteria (para. 33.4.1.4.4.3)
Low danger	Any substance which reacts slowly with water at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 1 litre per kilogram of substance per hour, and which does not meet the criteria for high and medium danger	UN Test N.5 Manual of Tests and Criteria (para. 33.4.1.4.4.4)

## 4.4 **Proposal for the definition of oxidizing substances and criteria for hazards levels for their classification**

### 4.4.1 *Definition*

Oxidizing substances are

- liquid or solid substances which, while in themselves not necessarily combustible, may, generally by yielding oxygen, cause, or contribute to, the combustion of other material;
- gases which may, generally by providing oxygen, cause, or contribute to, the combustion of other material more than air does.

**4.4.2 Criteria for hazard levels**

<b>Oxidizing substances (liquids)</b>		
<b>Hazard level</b>	<b>Criteria</b>	<b>Test methods</b>
High danger	Any substance which, in the 1:1 mixture, by mass, of substance and cellulose tested, spontaneously ignites; or the mean pressure rise time of a 1:1 mixture, by mass, of substance and cellulose is less than that of a 1:1 mixture, by mass, of 50% perchloric acid and cellulose	UN Test 0.2 Manual of Tests and Criteria (para. 34.4.2.4.2)
Medium danger	Any substance which, in the 1:1 mixture, by mass, of substance and cellulose tested, exhibits a mean pressure rise time less than or equal to the mean pressure rise time of a 1:1 mixture, by mass, of 40% aqueous sodium chlorate solution and cellulose; and the criteria for high danger are not met	UN Test 0.2 Manual of Tests and Criteria (para. 34.4.2.4.2)
Low danger	Any substance which, in the 1:1 mixture, by mass, of substance and cellulose tested, exhibits a mean pressure rise time less than or equal to the mean pressure rise time of a 1:1 mixture, by mass, of 65% aqueous nitric acid and cellulose; and the criteria for high and medium danger are not met	UN Test 0.2 Manual of Tests and Criteria (para. 34.4.2.4.2)



Oxidizing substances (solids)		
Hazard level	Criteria	Test methods
High danger	Any substance which, in the 4:1 or 1:1 sample-to-cellulose ratio (by mass) tested, exhibits a mean burning time less than the mean burning time of a 3:2 mixture, by mass, of potassium bromate and cellulose	UN Test 0.1 Manual of Tests and Criteria (para. 34.4.1.4.2)
Medium danger	Any substance which, in the 4:1 or 1:1 sample-to-cellulose ratio (by mass) tested, exhibits a mean burning time equal to or less than the mean burning time of a 2:3 mixture (by mass) of potassium bromate and cellulose and the criteria for high danger are not met	UN Test 0.1 Manual of Tests and Criteria (para. 34.4.1.4.2)
Low danger	Any substance which, in the 4:1 or 1:1 sample-to-cellulose ratio (by mass) tested, exhibits a mean burning time equal to or less than the mean burning time of a 3:7 mixture (by mass) of potassium bromate and cellulose and the criteria for high and medium danger are not met	UN Test 0.1 Manual of Tests and Criteria (para. 34.4.1.4.2)

Oxidizing substances (gases)	
Criteria	Test methods
Any gas which may, generally by providing oxygen, cause or contribute to the combustion of other material more than air does.	ISO 10 156: 1996 ( <i>NOTE: Improvement of this standard is under consideration by ISO; ISO target date for the revised standard is 2001</i> ).

## 4.5 Proposal for the definition of organic peroxides and criteria for their classification

### 4.5.1 Definition

Organic peroxides are liquid or solid organic substances which contain the bivalent -O-O- structure and may be considered derivatives of hydrogen peroxide, where one or both of the hydrogen atoms have been replaced by organic radicals.

**4.5.2 Criteria for classification**

<b>Organic peroxides</b>	
<b>Criteria</b>	<b>Test methods</b>
<p>Any organic peroxide, except organic peroxides or organic peroxides formulations:</p> <p>(a) containing not more than 1.0% available oxygen from the organic peroxides when containing not more than 1.0% hydrogen peroxide; or</p> <p>(b) containing not more than 0.5% available oxygen from the organic peroxides when containing more than 1.0% but not more than 7.0% hydrogen peroxide.</p> <p>Organic peroxides in packaged form may be classified under types A to G in accordance with the criteria of the Manual of Tests and Criteria, Part II</p> <p><i>NOTE 1: Type G is not dangerous for transport.</i></p> <p><i>NOTE 2: Sub-divisions may not be necessary for all systems.</i></p>	<p>Test series A to H (Refer to Part II of the Manual of Tests and criteria)</p>

**4.6 Proposal for the definition of self-reactive substances and criteria for their classification****4.6.1 Definition**

Self-reactive substances are thermally unstable liquid or solid substances liable to undergo a strongly exothermic decomposition even without participation of oxygen (air). This definition excludes organic peroxides and substances which are explosive or oxidizing.

#### 4.6.2 Criteria for classification

Self-reactive substances	
Criteria	Test methods
<p>Criteria of the Manual of Tests and Criteria, Part II. Self-reactive substances in packaged form may be classified under types A to G in accordance with those criteria</p> <p><i>NOTE 1: Type G is not dangerous for transport.</i></p> <p><i>NOTE 2: Sub-divisions may not be necessary for all systems.</i></p>	<p>Test series A to H (Refer to Part II of the Manual of Tests and criteria)</p>

#### 4.7 Proposal for the definition of explosives and criteria for their classification

##### 4.7.1 Definition

Solid or liquid substances (or mixtures of substances) which are in themselves capable by chemical reaction of producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings, including pyrotechnic substances.

Articles containing one or more explosive substances, except devices containing explosive substances in such quantity or of such a character that their inadvertent or accidental ignition shall not cause any effect external to the device either by projection, fire, smoke, heat or loud noise.

Substances or articles which are manufactured with the view to producing a practical explosive or pyrotechnic effect.

**NOTE:** A pyrotechnic substance is a substance or mixture of substances designed to produce an effect by heat, light, sound, gas or smoke or a combination of these as the result of non-detonative self-sustaining exothermic chemical reactions. Pyrotechnic substances are regarded as explosive substances even when they do not evolve gases.

A pyrotechnic article is an article containing one or more pyrotechnic substances.

**4.7.2 Criteria for classification**

<b>Explosive substances (liquid or solid) and explosive articles</b>	
<b>Tests and criteria</b>	<b>Comments</b>
Explosibility: according to UN Test series 2 (Section 12) <u>1/</u>	Intentional explosives <u>2/</u> are not subject to UN Test series 2
Sensitiveness: according to UN Test series 3 (Section 13) <u>1/</u> <u>3/</u>	<b>NOTE:</b> Explosive substances in packaged form and articles may be classified under divisions 1.1 to 1.6 and compatibility groups A to S to distinguish technical requirements.
Thermal stability: according to UN Test 3(c) (Sub-section 13.6.1) <u>1/</u>	

1/ See: UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria (ST/SG/AC.10/11/Rev.2, United Nations publication, Sales No. E.95.VIII.2).

2/ This comprises substances and articles which are manufactured with a view to producing a practical explosive or pyrotechnic effect.

3/ Explosive substances which do not meet the criteria for impact and/or friction sensitivity may be classified as explosives for some regulatory purposes.

**NOTE 1:** The use of the word "explosive" can have different meanings and interpretations. Reference to "an explosive" or "explosives" is commonly understood to mean substances or articles in Class 1 of the scheme of the UN Recommendations on the Transport of Dangerous Goods, that is those which are intentional explosives or have properties which when assessed under the test procedure of the Manual of Tests and Criteria place them in UN Class 1. The description "explosive" can, however, be used to describe a property and as such it encompasses a wider range of substances than just those in UN Class 1. The Global Harmonized System (GHS) requires that classification is based on intrinsic properties and the word 'explosive' in that context can be used to describe the property of a substance i.e. its ability to explode, as well as referring to a substance or article that has been designed to have explosive properties. This can lead to confusion and difficulty but in the above definition "explosive" refers to explosion hazard of substances and articles and is not limited to those which would be placed in Class 1 of the UN scheme.

**NOTE 2:** Some explosive substances are wetted with water or alcohols or diluted with other substances to suppress their explosives properties (Desensitized explosives). They may be treated differently from explosive substances for some regulatory purposes.

**4.8 Proposal for criteria for substances which are corrosive to metals**

<b>Hazard level</b>	<b>Criteria</b>	<b>Test method</b>
Low danger	Corrosion rate on steel or aluminium surfaces exceeding 6.25 mm a year at a test temperature of 55 °C.	For the purposes of testing steel, type P235 (ISO 9328 (II):1991) or a similar type, and for testing aluminium, non-clad types 7075-T6 or AZ5GU-T6 shall be used. An acceptable test is prescribed in ASTM G31-72 (Reapproved 1990).

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